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increased to compensate for decreasing amounts of outgassing from the coating chamber. The titanium oxide layer can have has an optical extinction coefficient between about 0.06 and 0.08 upon deposit, according to the present invention. --

IN THE CLAIMS

Cancel claim ~~1~~ without prejudice and insert following new claims 41-77.

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36C<sup>1</sup> 41. A method for producing a layer of titanium dioxide in at least the crystalline phase, wherein said layer of titanium dioxide is a photocatalytically-activatable self-cleaning coating over the glass float ribbon, and further wherein said coating is capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$  upon exposure to ultraviolet radiation, said method comprising the steps of:

positioning a chemical vapor deposition coating apparatus over a tin bath containing a glass ribbon having a temperature of at least about 400° C (752° F);

directing a titanium dioxide precursor through said chemical vapor deposition apparatus over a surface of the glass ribbon heated to said temperature; and

thereafter annealing the glass ribbon,

whereby said layer of titanium dioxide is produced.

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42. A method according to claim ~~41~~<sup>1</sup>, wherein the glass ribbon is at a temperature of at least about 538° C.

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43. A method according to claim ~~41~~<sup>1</sup>, wherein the glass ribbon is at a temperature of at least about 600° C.

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44. A method according to claim ~~41~~<sup>1</sup>, further comprising the step of exposing the photocatalytically-activatable self-cleaning coating to ultraviolet radiation whereby a photocatalytically-activated self-cleaning coating is produced.

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45. A method according to claim ~~41~~<sup>1</sup>, wherein the crystalline phase is at least anatase.

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46. A method for producing a glass sheet comprising a layer of titanium dioxide in at least the crystalline phase, wherein said layer of titanium dioxide is a photocatalytically-activatable self-cleaning coating, and further wherein said coating is capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$  upon exposure to ultraviolet radiation, said method comprising the steps of:

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positioning a chemical vapor deposition coating apparatus over a tin bath containing a glass ribbon having a temperature of at least about  $400^{\circ} \text{ C}$  ( $752^{\circ} \text{ F}$ );

directing a titanium dioxide precursor in a carrier gas stream through said chemical vapor deposition apparatus over a surface of the glass ribbon heated to said temperature; and

thereafter annealing the glass ribbon; and

producing a glass sheet from said annealed glass ribbon, whereby said glass sheet contains said layer of titanium dioxide.

7  
47. A method according to claim ~~46~~<sup>6</sup>, wherein the glass ribbon is at a temperature of at least about  $538^{\circ} \text{ C}$ .

8  
48. A method according to claim ~~46~~<sup>6</sup>, wherein the glass ribbon is at a temperature of at least about  $600^{\circ} \text{ C}$ .

9  
49. A method according to claim ~~46~~<sup>6</sup>, further comprising the step of exposing the photocatalytically-activatable self-cleaning coating to ultraviolet radiation whereby a photocatalytically-activated self-cleaning coating is produced.

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50. A method according to claim ~~46~~<sup>6</sup> wherein the directing of the titanium dioxide precursor is directly onto

the surface of the glass ribbon without any intervening coating layer.

<sup>11</sup>  
~~51~~. A method according to claim <sup>6</sup>~~46~~ wherein the at least crystalline phase of the titanium dioxide is selected from at least one of anatase, rutile, and brookite crystalline forms of titanium dioxide and wherein an amorphous phase of titanium dioxide may also be present.

<sup>12</sup>  
~~52~~. In a method for forming a glass float ribbon wherein the method includes the steps of melting glass batch materials in a furnace; delivering the molten glass onto a bath of molten tin; pulling the molten glass across the tin bath whereupon the glass is sized and controllably cooled to form a dimensionally stable glass float ribbon; removing the float ribbon from the tin bath; moving the float ribbon by conveying roller through a lehr to anneal the float ribbon; moving the float ribbon to a cutting station on conveying rollers where the ribbon is cut into glass sheets, the improvement comprising:

depositing over a surface of said float ribbon as the float ribbon is formed in said tin bath by chemical vapor deposition at least a crystalline phase of a photocatalytically-activatable self-cleaning coating,

whereby said glass sheets comprise said photocatalytically-activatable self cleaning coating.

<sup>13</sup>  
~~53~~. A method according to claim <sup>12</sup>~~52~~, further comprising the step of exposing said photocatalytically-activatable self-cleaning coating to ultraviolet radiation in order to provide a photocatalytically-activated self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

<sup>14</sup>  
~~54~~. A method according to claim <sup>12</sup>~~52~~, wherein said crystalline phase comprises titanium dioxide.

<sup>15</sup>  
~~55~~. A method according to claim <sup>12</sup>~~52~~, the improvement further comprising: depositing over a surface of said float ribbon as the float ribbon is formed in said tin bath a sodium ion diffusion barrier layer having a thickness of at least about 100 Å over a surface of said float ribbon and depositing in said tin bath said photocatalytically-activatable self-cleaning coating over said sodium ion diffusion barrier layer.

<sup>16</sup>  
~~56~~. A method according to claim <sup>12</sup>~~52~~ wherein said photocatalytically-activatable self cleaning coating has a thickness in the range of about 100 to 2500 Angstroms.

<sup>17</sup>  
~~57~~. A method according to claim <sup>16</sup>~~56~~, wherein said photocatalytically-activatable self cleaning coating has a thickness in the range of from about 100 to about 1000 Angstroms.

<sup>18</sup>  
~~58~~. A method according to claim <sup>17</sup>~~57~~, wherein said photocatalytically-activatable self cleaning coating has a thickness in the range of from about 100 to about 500 Angstroms.

<sup>19</sup>  
~~59~~. A method according to claim <sup>18</sup>~~58~~, wherein said photocatalytically-activatable self cleaning coating has a thickness in the range of from about 100 to about 400 Angstroms.

<sup>20</sup>  
~~60~~. A method according to claim <sup>19</sup>~~59~~, wherein said photocatalytically-activatable self cleaning coating has a thickness in the range of from about 100 to about 200 Angstroms.

<sup>21</sup>  
~~61~~. A method according to claim <sup>12</sup>~~52~~, the improvement further comprising: depositing a sodium ion diffusion barrier layer over a surface of said float ribbon as the float ribbon is formed in said tin bath, and depositing said photocatalytically-activatable self-cleaning coating over said

sodium ion diffusion barrier layer in said tin bath wherein the sodium ion diffusion barrier layer comprises at least one of amorphous and crystalline phase metal oxides selected from cobalt oxides, chromium oxides, iron oxides, tin oxides, titanium oxides, zirconium oxides, fluorine-doped tin oxides, aluminum oxides, magnesium oxides, zinc oxides, and super-oxides and sub-oxides of any of the foregoing.

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<sup>22</sup><sub>62</sub>. A method according to claim <sup>21</sup><sub>61</sub>, wherein the sodium ion diffusion barrier layer comprises at least one metal oxide selected from magnesium oxides, aluminum oxides, zinc oxides, tin oxides, and super-oxides and sub-oxides of any of the foregoing.

*56C2*  
63. A method according to claim 52, the improvement further comprising: depositing over a surface of said float ribbon as the float ribbon is formed in said tin bath a sodium ion diffusion barrier layer comprising silicone oxide and having a thickness of at least about 100 Å over a surface of said float ribbon and depositing in said tin bath said photocatalytically-activatable self-cleaning coating over said sodium ion diffusion barrier layer.

64. A method comprising the steps of:

providing by a float manufacturing process a glass article having at least one surface;

depositing in a tin bath during said float manufacturing process a photocatalytically-activatable self-cleaning coating over the surface of the article by chemical vapor deposition so that the coating has titanium dioxide in at least the crystalline phase and has a thickness ranging from at least 100 Å to less than 1 micron.

<sup>25</sup><sub>65</sub>. A method according to claim <sup>24</sup><sub>64</sub> wherein said photocatalytic reaction rate is determinable as the rate of removal of a stearic acid test film in the range of 100 to 200 Angstroms thick deposited over said photocatalytically-

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activatable self-cleaning coating wherein said photocatalytic reaction rate is quantitatively determinable as the slope of a curve formed by a plotting of a plurality of Fourier Transform Infrared Spectrophotometer measurements of the integrated intensity of carbon-hydrogen stretching vibrational absorption bands of the stearic acid test film versus an accumulated time of exposure of said photocatalytically-activatable self-cleaning coating to ultraviolet radiation of a frequency within the range of about 300 to 400 nanometers provided by an ultraviolet radiation source positioned over said photocatalytically-activatable self-cleaning coating and having an intensity of about 20 watts per square meter as measured at the surface of the photocatalytically-activatable self-cleaning coating.

<sup>26</sup>  
~~66~~. A method according to claim <sup>24</sup>~~64~~, further comprising the step of exposing the photocatalytically-activatable self-cleaning coating to ultraviolet radiation whereby a photocatalytically-activated self-cleaning coating having a photocatalytically-activated self-cleaning reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$  is produced.

<sup>27</sup>  
~~67~~. A method according to claim <sup>24</sup>~~64~~ wherein said process is selected from a chemical vapor deposition process wherein the article has a minimum temperature to provide sufficient decomposition of the titanium precursor.

<sup>28</sup>  
~~68~~. A process for the production of a titanium dioxide coating having a thickness ranging from about 100 to about 1000 Angstroms on a float glass ribbon, comprising:

manufacturing a continuous float glass ribbon having a first major surface and an opposite major surface defined as a second major surface;

positioning a chemical vapor deposition coating apparatus over the surface of the float ribbon at a point in a tin bath where the float ribbon has a temperature of at least about 400° C;

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directing a titanium metal oxide precursor through said chemical vapor deposition apparatus over a surface of the float ribbon in said tin bath, and

annealing the float ribbon

whereby a titanium dioxide coating comprising at least anatase and amorphous phases of titanium dioxide is produced, and wherein

the titanium dioxide coating is a photocatalytically-activatable self-cleaning coating.

*B110*  
<sup>29</sup>  
~~68~~. A process for the production of a titanium dioxide coating according to claim <sup>28</sup>~~68~~, wherein the photocatalytically-activatable self-cleaning coating is capable of having a photocatalytically-activated reaction rate of at least about  $2 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

<sup>30</sup>  
~~70~~. A process for the production of a titanium dioxide coating according to claim <sup>28</sup>~~68~~, wherein the float ribbon has a temperature ranging from about 538° to less than about 800° C.

<sup>31</sup>  
~~71~~. A process for the production of a titanium dioxide coating according to claim <sup>28</sup>~~68~~, wherein said coating is physically durable.

<sup>32</sup>  
~~72~~. A process for the production of a titanium dioxide coating according to claim <sup>28</sup>~~68~~, wherein said coating is resistant to chemical attack.

<sup>33</sup>  
~~73~~. A process for the production of a titanium dioxide coating according to claim <sup>28</sup>~~68~~, wherein the photocatalytically-activatable self-cleaning coating is capable of having a photocatalytically-activated self-cleaning reaction rate of at least about  $5 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

<sup>34</sup>  
~~74~~. A process for the production of a titanium dioxide coating according to claim <sup>28</sup>~~68~~, wherein the photocatalytically-activatable self-cleaning coating is capable of having a

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photocatalytically-activated self-cleaning reaction rate of at least about  $7.79 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

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75. A process for the production of a titanium dioxide coating according to claim 38, wherein the photocatalytically-activatable self-cleaning coating is capable of having photocatalytically-activated self-cleaning reaction rate of at least about  $12.29 \times 10^{-3} \text{ cm}^{-1} \text{ min}^{-1}$ .

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76. A method comprising the steps of:  
providing by a float glass manufacturing process a glass article having at least one surface;  
depositing a sodium ion diffusion barrier coating over the surface of the article by chemical vapor deposition in a tin bath during the glass manufacturing process; and  
depositing at a temperature in the range of from about  $538^\circ$  to below about  $800^\circ \text{ C}$  ( $1000^\circ$  to  $1472^\circ \text{ F}$ ) a photocatalytically-activatable self-cleaning coating over the barrier coating so that the photocatalytically-activatable self-cleaning coating comprises titanium dioxide in at least the crystalline phase and has a thickness ranging from at least about  $100 \text{ \AA}$  to less than 1 micron.

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77. A method according to claim 36, wherein the photocatalytically-activatable self-cleaning coating is deposited at a temperature ranging from  $554^\circ$  to less than about  $800^\circ \text{ C}$  ( $1029^\circ$  to  $1472^\circ \text{ F}$ ).